

STUDIES ON OVERVOLTAGE, IX

**The Nature of Cathode and Anode Discharge
Potentials at Several Metal Surfaces**

A DISSERTATION

**Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the University of Michigan**

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S. KLEINHEKSEL
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STUDIES ON OVERVOLTAGE. IX

THE NATURE OF CATHODE AND ANODE DISCHARGE POTENTIALS AT SEVERAL METAL SURFACES^{1,2}

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Polarization potentials have been measured, in general, by two methods commonly known as the direct and the commutator methods. Early investigators invariably found that the direct method gave higher values than the commutator method. For more than half a century the correct explanation has been sought for this discrepancy. The explanations offered fall largely into two groups. According to one group, the difference between the values given by the two methods is due to the existence of a resistance of some nature at the interface between electrode and electrolyte. This resistance has been named by different authors "surface resistance," "transfer resistance," "contact resistance," "film resistance," etc. According to the other group, the interrupting device used in connection with the commutator does not permit the total discharge potential to be measured because of the very rapid drop in potential during the interval between interruption of the current and measurement of the potential. Several years ago a thorough investigation of this subject was started in this laboratory. A brief summary of the work follows.

In the first paper (6) it was proven that the commutator gives values which are only averages. This provided a possible explanation for the observed discrepancies between the two methods since the commutator, therefore, could never give, directly, values as high as those obtained by the direct method.

In the second paper (7) a commutator of special design was used in an attempt to show that the potential at the beginning of the discharge interval is the same as that at the end of the charge interval. This was

¹ This paper is a portion of the dissertation submitted by Stanley Kleinheksel to the Faculty of the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² The oscillograph used in these investigations was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

not entirely successful, since it was not possible to measure the discharge potential at the instant the polarizing circuit was opened, and since the potential was dropping very rapidly at this time.

In the third paper (1) a new commutator was used that permitted charge potentials and corresponding discharge potentials to be measured within 0.0003 sec. from the time of interruption of the polarizing circuit. There was still, however, a discrepancy of a few millivolts between the measured potentials at the end of charge and the beginning of discharge. Certain other difficulties were also discovered that are inherent in the regular commutator potentiometer method and render it undesirable for the measurement of overvoltage and transfer resistance.

In the fourth paper (2) a commutator was used that permitted potentials to be measured practically simultaneously at several points during both the charge and discharge intervals. These results gave curves which could be extrapolated apparently with a high degree of accuracy to the instant of interruption of the polarizing circuit. The curves indicated that for platinized platinum in 2 *N* sulfuric acid at current densities between 3.8 and 150 ma. there is no surface resistance, but for smooth platinum the decrease in potential was so rapid as to make extrapolation highly uncertain.

The fifth paper (3) contains the description of a new device for the study of polarization potentials, known as a commutator oscillograph system. Actual photographs of the charge and discharge potentials throughout the complete cycle were obtained. This proved to be an excellent means for making a direct comparison of the commutator and direct methods. Oscillograms were taken by both the direct and commutator methods on the same film and practically at the same time and thus under identical conditions. These curves showed that the commutator gives a maximum value for charge potential that is identical with the value given by the direct method and confirmed the statement made in the second paper (7) that "the commutator and the direct methods would give the same values if measurements by the commutator method could be made at the instant the polarizing current is interrupted." The curves show, however, that for current densities of the order of 0.02 amp. it requires about 0.008 sec. for the cathode and 0.04 sec. for the anode to reach a maximum value. This means that, if the commutator is rotated at a speed too high to allow these time intervals for charge, correct values for charge will not be obtained. Investigators up to this time have generally used such high speeds in order to prevent the very rapid loss in potential at the beginning of discharge.

Those who support the idea that a resistance of some kind exists at the contact surface between electrode and electrolyte base their conclusions

upon the presence of an instantaneous drop in electrode potential immediately after the polarizing circuit is opened. This point of view is probably best represented by the work of Newbery (8) in which he used a cathode-ray oscillograph. He states, "The existence of this gap (a vertical displacement between charge and discharge curves) proves conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted. . . . This resistance—transfer resistance—may be measured by observing the vertical height of the gap in the curves." In the seventh paper (4) an electromagnetic interrupter was substituted in place of the commutator. With this it was possible to determine the true nature of the decay curves by superimposing them directly upon another curve known to be due to an I.R. drop only, or on one known to be due to both an I.R. drop and the decay of a true electrode potential. It was evident, clearly, from the comparisons made of this nature, that there is no surface resistance at *platinized platinum* electrodes in 2 *N* sulfuric acid for current densities up to 0.017 amp.

In the eighth paper (5) the same method was used to study the nature of polarization phenomena at *smooth platinum* electrodes. It was found, however, that the early part of the potential decay curve dropped so rapidly that it could not be distinguished from a drop due to a pure resistance. It could not be demonstrated, therefore, that for such electrodes there is no surface resistance.

In the present investigation new equipment has been used with which it is possible to distinguish definitely between an I.R. drop and an electrode potential decay even for smooth platinum and several other materials investigated. With this equipment the decay of a true electrode potential may be distinguished from an I.R. drop in any case where the former requires more than 1×10^{-5} sec. per millivolt change in potential.

Overvoltage decay curves at the cathode were obtained for platinized platinum, smooth platinum, palladium, gold, silver, zinc, cadmium, antimony, and nickel. Decay curves at the anode were made for the first four. In each case curves were obtained at several current densities.

The method employed is fundamentally the same as that described in the last two papers (4, 5). In the present work, in order to be able to distinguish definitely in all cases between an I.R. drop and a true electrode potential decay, a new oscillograph vibrator (galvanometer) was used having a greatly increased frequency. In order to retain the desired sensitivity it was then necessary to construct a new amplifier having a much greater amplification; in fact, the sensitivity of the present system is actually 2.5 times that used previously.

The procedure is, essentially, to charge the cell under investigation for any desired period, then to interrupt the charging circuit at a definite

instant by means of an electromagnet, and finally to record the decay of potential photographically with the oscillograph. No current is drawn from the electrode under investigation.

The cell assembly is represented in figure 1 and needs no explanation except to state that the electrodes have an area of 1 sq. cm. and the backs are covered with paraffin.

It was found desirable to be able to obtain several sensitivities from the one amplifier. This was accomplished through a variation in the potential on the suppressor grid, G2, of the R.C.A. 57 tube (figure 2). Each different voltage value applied to the grid G2 required, however, a corresponding definite potential for grid G4 of the 2A3 tube. Six different combinations of voltages were used for grids G2 and G4, giving as many amplifier sensitivities designated as systems I, II, III, etc.; the first system produced the largest and the sixth the smallest sensitivity.

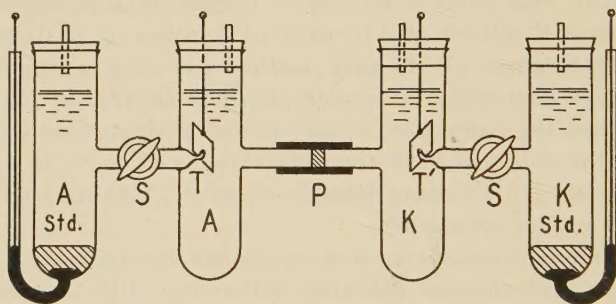


FIG. 1. Cell assembly

Each of the six systems required a separate calibration curve. A known potential E_g from a potentiometer applied to the control grid G1 of the amplifier, i.e., to the input leads (figure 2), produced a definite current I_p indicated by a milliammeter in the output circuit. A linear relation was found in the E_g - I_p curve between 60 and 130 ma. In order to locate the upper limit of the linear portion of the curve, it was only necessary, therefore, that the sum of all the potential differences in the input circuit should have a value such that the corresponding plate current was 130 ma. The oscillograph used required only 65 ma. for full scale deflection, which is well within the linear relationship. The upper limit of the linear portion for each amplification curve, in terms of milliamper output, and the approximate sensitivity in terms of millivolts per milliamper is given in table 1 for the six systems. The table contains, also, the corresponding E_{g2} and E_{g4} potentials.

A simplified diagram of the complete apparatus is given in figure 3. A potential divider, V, supplies the current for charging the electrodes. This circuit contains the cell under investigation and a standard 10-ohm

resistance, and is closed through contacts B3 -- B4 of electromagnet B. The value of the charging current is obtained from the measured potential drop across the standard resistance. Switch E represents a group of the four electrodes,—anode standard, anode, cathode, or cathode standard,—

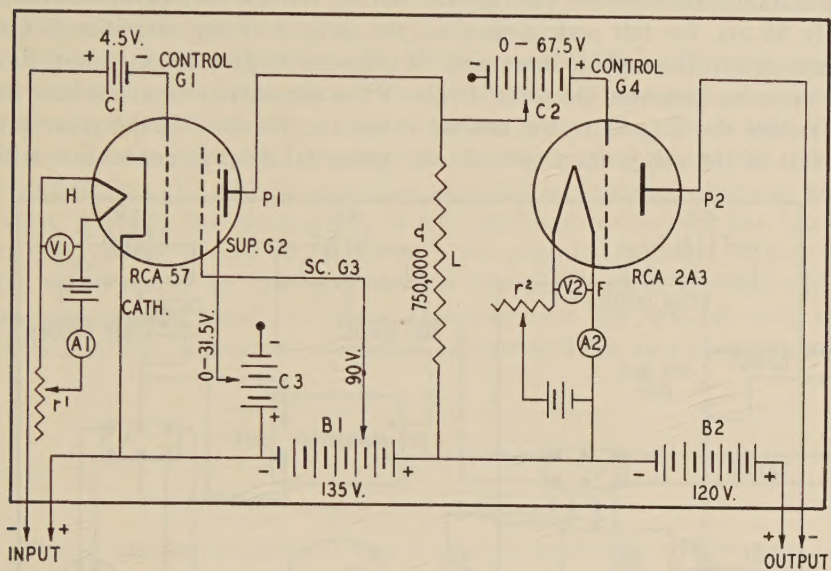


FIG. 2. D. C. amplifier

TABLE 1
Constants for the six amplification systems

SYSTEM NO.	Eg2	Eg4	OUTPUT CURRENT	APPROXIMATE SENSITIVITY
	<i>volts</i>	<i>volts</i>	<i>ma.</i>	<i>mv. per ma.</i>
I.....	0.0	67.5	130	1.0
II.....	-16.5	22.5	125	2.3
III.....	-25.5	10.5	120	4.5
IV.....	-28.5	6.0	120	7.3
V.....	-30.0	3.0	105	9.4
VI.....	-31.5	0.0	100	12.7

may be applied to either the potentiometer or the input of the amplifier. By means of the potential divider, V1, a potential may be placed in series with that of the cell under investigation. Since the potential to be measured is fixed, it is necessary to have this auxiliary potential from V1 in order to bring the current in the output circuit to the value corresponding to the upper limit of the linear portion of the characteristic curve of the

amplifier for the particular amplification system being used, i.e., 130 ma. for system I.

The output of the amplifier may be connected through switch A to either milliammeter Am or to the sensitive element of the oscillograph. Since the linear portion of the characteristic curve of the amplifier, for system I for instance, lies between 130 ma. and 60 ma., but the oscillograph requires only 65 ma. for full scale deflection, the output of the amplifier is first connected to the milliammeter and V1 adjusted to give 130 ma., and then an opposing potential from the divider V2 in the output circuit is inserted to reduce the current to the desired value, i.e., 65 ma. If the polarizing circuit of the cell is then opened, any potential drop in connection with

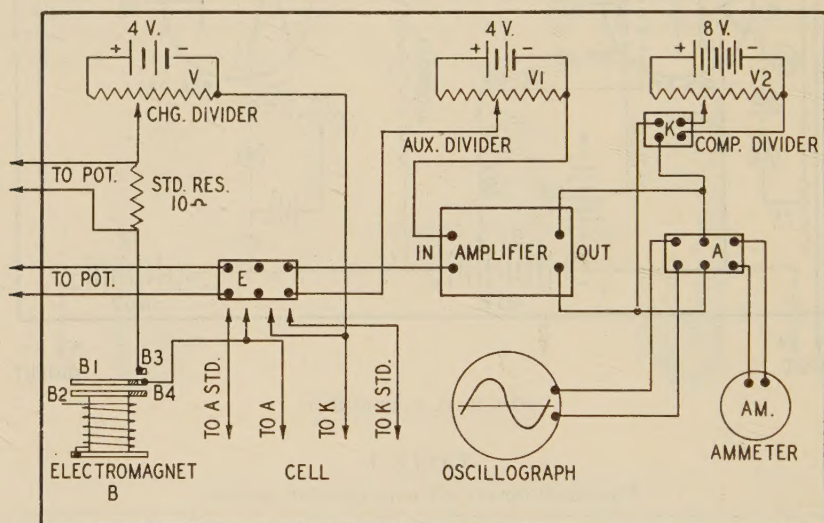


FIG. 3. Simplified diagram of apparatus

this cell and included in the input potential of the amplifier results in a decrease in plate current along the linear portion of the characteristic curve starting from 130 ma., but appears on the ammeter as a corresponding decrease from 65 ma. After such preliminary adjustments the ammeter is replaced by the oscillograph, which produces a permanent record upon the rotating film.

The resistances of the milliammeter and the oscillograph element are nearly equal, so that no change in total resistance of the circuit is made when one is replaced by the other. Since the element of the oscillograph is in series with a portion of the potential divider V2, however, the resistance of the latter must be large compared to the former in order that the current change in the output circuit of the amplifier may be truly represented by the deflection of the oscillograph element. At no time was the

resistance included in the potential divider less than 200 times the resistance of the element. Experiments were carried out using various compensating potentials to shift the recorded curve to different positions from top to bottom of a calibrated film, and the potential indicated was entirely independent of the compensating potential, showing that the oscillograph records the true potential of the cell irrespective of the value of V2 used and therefore the position of the curve on the film.

In order to convert deflections of the light beam of the oscillograph which are recorded on the photographic film into volts, it is necessary to calibrate such recorded deflections in terms of applied potentials. To do this, first 60 mv. were applied from a potentiometer in the place of the cell. The potentials from V1 and V2 were then adjusted as described above to give 65 ma. through the oscillograph, which produced a line near the top of the film. With V1 and V2 left constant, the potential from the potentiometer was reduced 15 mv. and another line produced on the film which appeared slightly below the first. This operation was repeated until the whole film was calibrated. Separate calibrated films were made for each

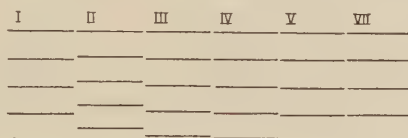


FIG. 4. Samples of calibrated films for the six amplification systems used

of the six amplification systems used. Samples of such films are shown in figure 4. New calibrations had to be made occasionally, owing to changes in the characteristics of the amplifier.

In all experiments the electrodes had an approximate exposed area of 1 sq. cm. and the back of the electrode was covered with paraffin. The electrolyte was 2 *N* sulfuric acid, which has a hydrogen-ion activity of nearly 1. Electrolysis was allowed to proceed for about one hour before measurements were taken. By this time the potentials had reached a constant value, the anode chamber had become saturated with oxygen and the cathode with hydrogen, and all other gases had been swept out.

Five different potentials were measured for each system used: anode vs. anode standard (A), anode vs. cathode standard (Ai), anode standard vs. cathode standard (I), cathode vs. cathode standard (K), and cathode vs. anode standard (Ki). The first gives the actual potential of the anode, the second gives this potential plus the I.R. drop through the solution, the third the I.R. drop through the solution alone, the fourth the actual cathode potential, and the fifth the cathode potential plus the I. R. drop through the solution.

The first electrodes worked with were platinized platinum. The

various decay curves are shown in figures 5 and 6. The only difference between the systems represented in the two figures is in current density. Several other current densities were used, but these are typical of all.

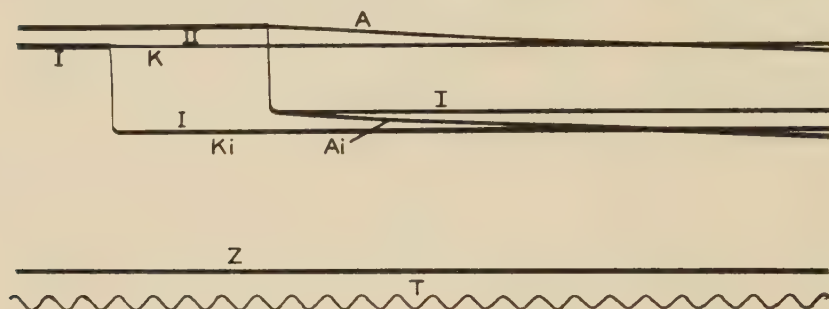


FIG. 5. Overvoltage decay curves for platinized platinum electrodes.
Amplifier system I

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.616	0.485
Ai	Anode vs. cathode standard	1.637	0.485
K	Cathode vs. cathode standard	0.008	0.485
Ki	Cathode vs. anode standard	0.029	0.485
I	Anode standard vs. cathode standard	0.021	
Z	Zero line of vibrator		

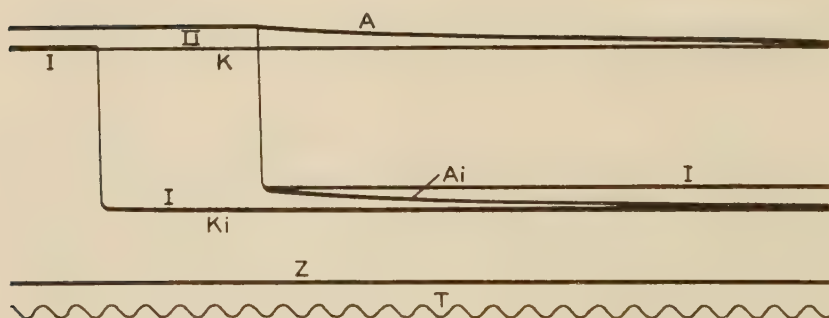


FIG. 6. Overvoltage decay curves for platinized platinum electrodes.
Amplifier system VI

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.840	9.05
Ai	Anode vs. cathode standard	2.336	9.05
K	Cathode vs. cathode standard	0.043	9.05
Ki	Cathode vs. anode standard	0.540	9.05
I	Anode standard vs. cathode standard	0.497	9.05
Z	Zero line of vibrator		

On each film there are two groups of curves, I and II, each made up of three curves. For instance, group II of figure 5 contains the curves A, Ai, and I. These are all superimposed at the start by the proper adjustment of V2. The point of separation of the curves represents the instant at which the polarizing current for the cell under investigation is interrupted. By means of various contact points on the rotating film drum this can be located at any desired time during the rotation of the film. One exposure is made to record the potential represented by A, another for Ai, and another for I. Group I is a similar set for the cathode. The base line for the undeflected vibrator element is represented by Z. The curve T represents a 120-cycle circuit. The films represented in these

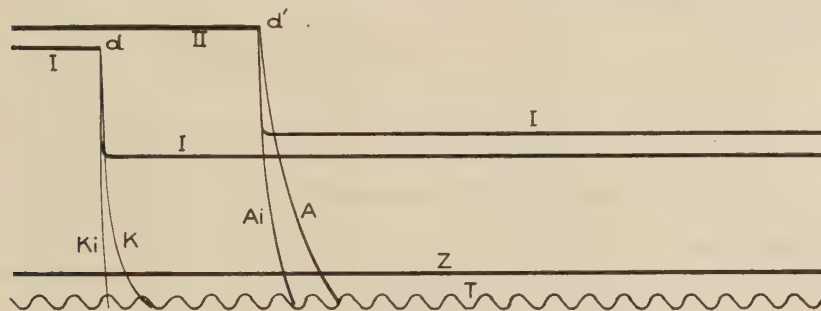


FIG. 7. Overvoltage decay curves for smooth platinum electrodes.
Amplifier system I

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.970	0.30
Ai	Anode vs. cathode standard	1.996	0.30
K	Cathode vs. cathode standard	0.107	0.30
Ki	Cathode vs. anode standard	0.133	0.30
I	Anode standard vs. cathode standard	0.026	
Z	Zero line of vibrator		

figures were, therefore, exposed eight times. In general the film speed was adjusted so that 1 mm. on the original film represents about 0.0007 sec.

In all cases the curve I represents a pure I.R. drop; it is the I.R. drop through the solution and may be measured by the potentiometer while the polarizing current is flowing. The value so measured agrees almost perfectly with the value calculated from a comparison of the drop in the I curve with the calibrated film. The curve A represents the decay of anode potential. It is to be noted that this decay is slow throughout its entire length, giving no indication of an I.R. drop. Curve Ai is the sum of the potentials represented by A and I, and shows the nature of a potential decay curve that does contain, also, a potential due to an I.R. drop. These curves indicate that the overvoltages, both at anode and cathode,

are very small at these current densities, and that there is no I.R. drop through any kind of film at the electrodes.

Curves for smooth platinum are shown in figures 7 and 8. In agreement with previous findings in this laboratory, the initial overvoltage decay for smooth platinum is far more rapid than for platinized platinum. However, in contrast to the earlier work, in which the decay curves for the electrode potentials could not be distinguished from an I.R. drop, it is clearly evident from these figures that the present equipment is capable of making this separation. Both the anode and the cathode potentials, curves A and K respectively, diverge from the vertical line I, which is due

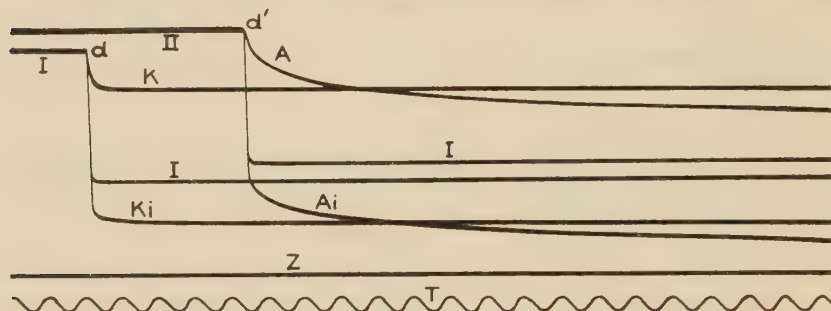


FIG. 8. Overvoltage decay curves for smooth platinum electrodes.
Amplifier system VI

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	2.075	7.26
Ai	Anode vs. cathode standard	2.481	7.26
K	Cathode vs. cathode standard	0.162	7.26
Ki	Cathode vs. anode standard	0.569	7.26
I	Anode standard vs. cathode standard	0.406	7.26
Z	Zero line of vibrator		

to a pure I.R. drop, from the instant the polarizing current is interrupted. This appears to be conclusive evidence for the non-existence of a potential drop due to transfer resistance or any other resistance even at smooth platinum electrodes. These curves show, also, that the initial rate of overvoltage decay for smooth platinum electrodes is slower at the anode than at the cathode.

When comparing the curves in different figures one must be sure to take into account the particular amplification system used. For the comparison factors see table 1.

The behavior of a palladium electrode during electrolysis differs from platinum in many respects. When a fresh palladium electrode, or one which has been used previously as an anode, is polarized cathodically,

electrolysis must be continued during several hours at a current density of several milliamperes before a visible evolution of hydrogen occurs. With the appearance of hydrogen bubbles the cathode potential rises rapidly to a definite value. After an electrode has been used as a cathode it may be removed from the electrolyte for several hours, and if it is again polarized cathodically hydrogen evolution will begin almost immediately, followed by a rapid rise of potential to the normal overvoltage value.

Overvoltage decay curves for a palladium cathode at several current densities are shown in figure 9. These curves drop very rapidly to what appears to be a constant value, which would be explained if a compound of hydrogen were formed at the palladium cathode. It should be remembered

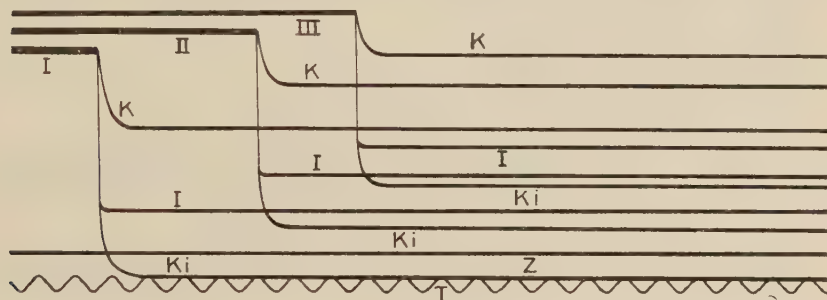


FIG. 9. Overvoltage decay curves for a palladium cathode at several current densities

Curve	Potential measured	Group I, system I	Group II, system II	Group III, system III
K	Cathode vs. cathode standard	0.046 v.	0.062 v.	0.081 v.
Ki	Cathode vs. anode standard	0.086 v.	0.143 v.	0.232 v.
I	Cathode standard vs. anode standard	0.040 v.	0.082 v.	0.152 v.
Current density		1.0 ma.	2.08 ma.	3.85 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

that these experiments were designed to study the character of the extremely rapid initial drop of potential at the beginning of the discharge and that, therefore, the photographs were taken at high speeds. If a low speed were used a curve having a definite but small downward slope extending to the normal hydrogen value might be obtained. This matter is under investigation at the present time.

A comparison of the K curves with the vertical portion of the I curves proves that no surface resistance exists at the cathode-electrolyte interface.

The behavior of a palladium anode during electrolysis is similar to that of a cathode. A new electrode, or one which has been used previously as a cathode, requires several hours before visible oxygen bubbles appear. Prolonged electrolysis results in a tarnishing of the surface.

Curves representing the anodic overvoltage decay for palladium are given in figure 10. The anode curves, A, slope gradually downward throughout the time of the exposure in contrast with corresponding curves for the cathode, where a rapid initial drop is followed by a very slow change. The overvoltage at the anode is much larger than at the cathode.

Curves for gold as cathode are represented in figure 11 and as anode in figure 12. Again the anode overvoltage is much greater than the cathode. Upon prolonged electrolysis the gold anode is tarnished to a dull chocolate color.

The cathode decay curves for silver are shown in figure 13. Reproducible curves could not be obtained for silver as anode.

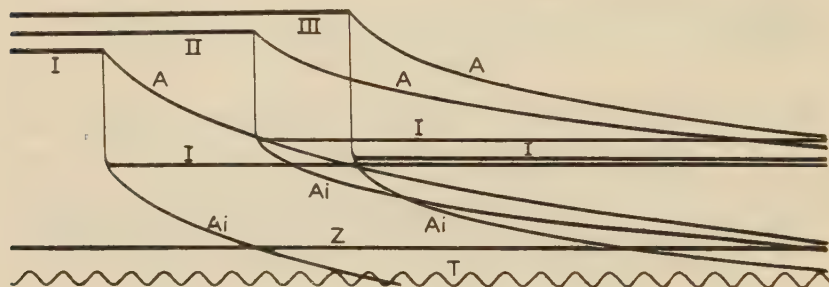


FIG. 10. Overvoltage decay curves for a palladium anode

Curve	Potential measured	Group I, system II	Group II, system III	Group III, system III
A	Anode vs. anode standard	1.842 v.	1.864 v.	1.873 v.
Ai	Anode vs. cathode standard	1.909 v.	1.991 v.	2.044 v.
I	Anode standard vs. cathode standard	0.068 v.	0.126 v.	0.171 v.
Current density		1.70 ma.	3.18 ma.	4.37 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

Zinc under ordinary conditions displaces hydrogen from 2 *N* sulfuric acid solution. Preliminary cathodic polarization of pure zinc, followed by buffing with clean cotton, results in a smooth surface which is passive. In most cases an electrode treated in this manner may be used as a cathode for hours without showing any tendency toward solution. Overvoltage curves for zinc as cathode are given in figure 14. Zinc shows an extremely rapid initial drop and then remains nearly constant.

The curves for cadmium are given in figure 15. These curves show that cadmium has an unusually high overvoltage, a large part of which disappears very rapidly.

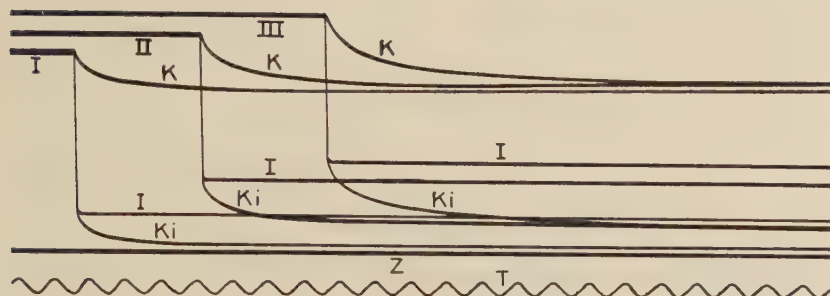


FIG. 11. Overvoltage decay curves for gold cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.491 v.	0.485 v.	0.484 v.
Ki	Cathode vs. anode standard	1.003 v.	0.831 v.	0.747 v.
I	Cathode standard vs. anode standard	0.512 v.	0.346 v.	0.263 v.
Current density		12.26 ma.	8.87 ma.	6.75 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

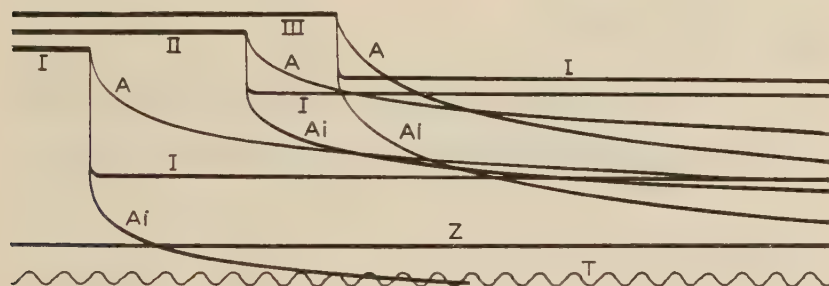


FIG. 12. Overvoltage decay curves for gold anode

Curve	Potential measured	Group I, system III	Group II, system III	Group III, system II
A	Anode vs. anode standard	2.046 v.	2.027 v.	2.010 v.
Ai	Anode vs. cathode standard	2.196 v.	2.096 v.	2.044 v.
I	Anode standard vs. cathode standard	0.150 v.	0.069 v.	0.034 v.
Current density		2.9 ma.	1.38 ma.	0.73 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

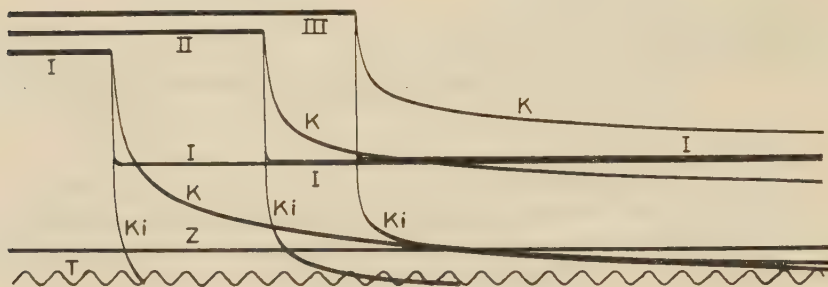


FIG. 13. Overvoltage decay curves for silver cathode

Curve	Potential measured	Group I, system III	Group II, system IV	Group III, system V
K	Cathode vs. cathode standard	0.480 v.	0.506 v.	0.520 v.
Ki	Cathode vs. anode standard	0.609 v.	0.749 v.	0.873 v.
I	Cathode standard vs. anode standard	0.128 v.	0.243 v.	0.348 v.
Current density		2.40 ma.	4.4 ma.	6.5 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

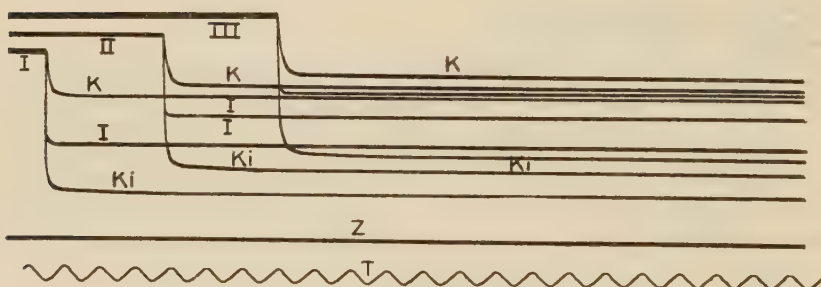


FIG. 14. Overvoltage decay curves for zinc cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.985 v.	0.942 v.	0.939 v.
Ki	Cathode vs. anode standard	1.302 v.	1.150 v.	1.086 v.
I	Cathode standard vs. anode standard	0.317 v.	0.205 v.	0.147 v.
Current density		7.15 ma.	4.62 ma.	3.33 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

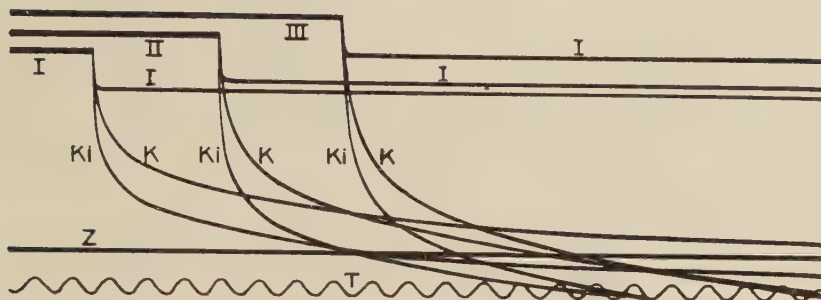


FIG. 15. Overvoltage decay curves for cadmium cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	1.117 v.	1.116 v.	1.078 v.
Ki	Cathode vs. anode standard	1.234 v.	1.210 v.	1.149 v.
I	Cathode standard vs. anode standard	0.117 v.	0.094 v.	0.071 v.
Current density		3.0 ma.	2.42 ma.	1.79 ma.

Z Zero line of sensitive vibrator

T 120-cycle timing curve

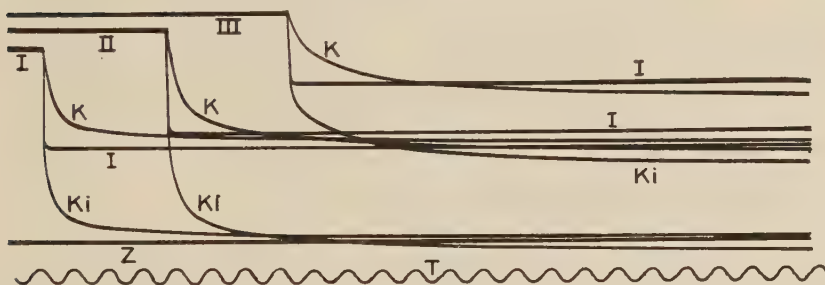


FIG. 16. Overvoltage decay curves for antimony cathode

Curve	Potential measured	Group I, system III	Group II, system II	Group III, system I
K	Cathode vs. cathode standard	0.615 v.	0.579 v.	0.525 v.
Ki	Cathode vs. anode standard	0.731 v.	0.641 v.	0.544 v.
I	Cathode standard vs. anode standard	0.116 v.	0.062 v.	0.019 v.
Current density		2.94 ma.	1.55 ma.	0.46 ma.

Z Zero line of sensitive vibrator

T 120-cycle timing curve

Cathode curves for antimony and nickel are shown in figures 16 and 17, respectively.

In every case studied the decay curves diverge from the corresponding I.R. drop curves immediately. These facts show conclusively that no part of the overvoltage decay is as rapid as an I.R. drop and, therefore, the possibility of the inclusion of a potential drop through some kind of resistance at the electrode solution interface in the measured electrode potential is excluded.

From a careful analysis of the cathode decay curves presented here and many others not included in this paper, it appears probable that at least

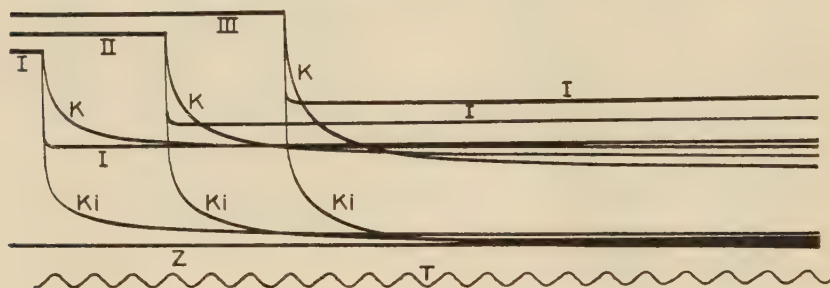


FIG. 17. Overvoltage decay curves for nickel cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.520 v.	0.509 v.	0.494 v.
Ki	Cathode vs. anode standard	0.817 v.	0.723 v.	0.656 v.
I	Cathode standard vs. anode standard	0.297 v.	0.214 v.	0.162 v.
Current density		5.72 ma.	4.09 ma.	3.1 ma.

Z Zero line of sensitive vibrator

T 120-cycle timing curve

two different causes are responsible for the total measured overvoltage. The first of these appears as an extremely rapid potential drop which, for most materials studied, is completed in less than 0.01 sec. This extremely rapid initial drop is followed by a slow decay, probably to the value of the normal hydrogen electrode. Only the initial rapid drop and the first portion of the slow decay were investigated in this research; thus it is not possible to arrive at conclusions regarding the later stages of the slow decay.

The value of the total hydrogen overvoltage increases with current density for all the materials used. The value of the initial rapid drop also increases with current density; but the residual overvoltage, i.e., the difference between the total overvoltage and that represented by the initial

rapid drop, is nearly constant for a given metal and is independent of current density. This is the first time that such an observation has been noted, because it is the first time that it has been possible to measure the very rapid initial overvoltage drop. Values for the initial overvoltage, the residual overvoltage, and total overvoltage are collected in table 2. This table contains data, also, from several curves not included in this paper. The variation of initial overvoltage with current density is evident from the values in column 3, and the constancy of residual overvoltage is evident from column 5. Both types of overvoltage depend to a pronounced degree upon the material used as electrode.

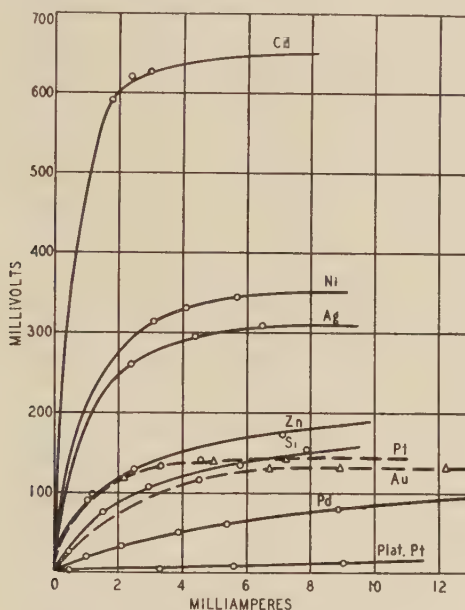


FIG. 18. Initial rapid overvoltage drop vs. current density

Curves showing the relation between current density and the overvoltage corresponding to the early rapid drop, data for which are contained in columns 1 and 3 of table 2, are given in figure 18. It is assumed that this type of hydrogen overvoltage is zero at zero current density and thus all the curves pass through the origin. These curves show considerable regularity, but no special significance is attached to them by the authors.

It is interesting to consider the data in this paper in the light of modern theories of overvoltage. The most interesting recent experimental work has been done by Bowden and coworkers. Bowden based his theory of overvoltage upon results obtained within the range of current densities from 10^{-8} to 10^{-3} amp. per square centimeter. Using a mercury electrode and

TABLE 2
Summary of hydrogen overvoltage values

CATHODE	(1) CURRENT DENSITY	(2) TOTAL OVER- VOLTAGE	(3) INITIAL OVERVOLT- AGE DROP	(4) PER CENT OF TOTAL	(5) RESIDUAL OVER- VOLTAGE
	<i>ma.</i>	<i>mv.</i>	<i>mv.</i>		<i>mv.</i>
Platinized platinum.....	0.485	8	0	20	8
	3.32	29	4		25
	5.58	38	7		31
	9.05	43	13		30
Smooth platinum.....	2.20	140	120	86	20
	5.02	162	138		24
	7.26	162	142		20
Palladium.....	1.00	46	20	65	26
	2.08	62	33		29
	3.85	81	52		29
	5.43	93	61		32
	8.94	111	79		32
	13.54	127	95		32
Gold.....	6.75	484	128	26	356
	8.87	485	126		359
	12.26	491	131		360
Silver*.....	2.40	480	260	57	220
	4.40	506	295		210
	6.50	520	310		210
Zinc.....	1.05	897	92	14	805
	1.24	901	97		804
	2.84	939	127		812
	3.33	939	129		810
	4.62	942	140		802
	7.15	985	175		810
Cadmium*.....	1.79	1078	590	55	488
	2.42	1116	620		496
	3.00	1117	625		492
Antimony.....	0.460	525	27	17	498
	1.55	579	75		504
	2.95	615	105		510
	4.55	617	117		500
	5.80	632	135		497
	7.88	652	154		498
Nickel.....	3.10	494	315	65	179
	4.09	509	332		177
	5.72	520	346		174

* Curves still have a distinct slope. Values correspond to a time one-sixth of a second after the interruption of the charging circuit.

a current density of 0.04 ma. he reported that there was no rapid initial drop in the cathode decay curve, but only a gradual drop from the moment the charging current was interrupted. In the light of the data presented in table 2 of the present paper this would be expected, since, at the current density used, probably only the type of overvoltage included in column 5 is effective.

In the same paper Bowden found that at current densities between 10^{-8} and 10^{-4} amp., $n = a + b \log i$, where n is the overvoltage, i the current density, and a and b are constants. Within this current density range, b was found to equal 0.120. At higher current densities, roughly 10^{-4} to 10^{-3} amp., the relation became $n = a + 2b \log i$. The data in table 2 offer a qualitative explanation for these observations. Within the range of low current densities, where the relation is $n = a + b \log i$, only the residual type of overvoltage corresponding to values in column 5 is effective; in the higher range of current densities both types of overvoltage represented by columns 3 and 5 are increasing simultaneously, giving a constant for b about twice the former. This explanation is supported by the fact that the portion of the cathode decay curve between the rapid initial drop and the subsequent slow decay shows a gradual change in slope, as would be expected if two potential drops, one rapid and one slow, were superimposed. The type of overvoltage represented by the values in column 3 appears at current densities above about 10^{-4} amp., and therefore was not studied or recognized by Bowden. At these high current densities the logarithmic relation does not hold, the overvoltage changing less rapidly with current density.

Bowden and Rideal assumed a difference between the apparent and "accessible area" of a metal surface to explain the difference in the quantities of electricity required to cause an equal increase in overvoltage at different metal electrodes having the same apparent area. For instance, they found that the "accessible area" of a platinized platinum electrode was as much as 2000 times the apparent or regularly measured area. Yet, in developing their relations between overvoltage and current density they used the apparent area, as have all previous workers in attempts to develop such relationships. If there is the great variation between the actual, effective, or accessible area and the geometric area, which is the only one that can be accurately measured, it appears to the authors that relationships such as above expressed between overvoltage and the geometric area should have no significance.

Probably the most plausible theory of overvoltage, based upon experiment, is the dipole theory proposed by Bowden. It was developed, however, with the aid of data obtained at current densities below those employed in this research. It is not surprising, therefore, that the data

submitted here do not fit well into his theory. They do show conclusively that his theory as postulated cannot be complete.

Probably the most promising theory of overvoltage from a theoretical point of view is based upon the recent considerations of Butler, Gurny, Fowler, and their associates, in which attempts are made to interpret electrode phenomena including overvoltage by the application of quantum mechanics.

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